

CATALYTIC CONVERSION OF BIOMASS DERIVED  
SYNTHESIS GAS TO DIESEL FUEL IN A SLURRY REACTOR

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INTRODUCTION

A project has been under investigation for several years at Arizona State University (ASU) with the objective of producing transportation grade liquid hydrocarbon fuel from a wide variety of biomass type feedstocks. The intended product is the equivalent of that derived from petroleum. Thus a renewable and/or waste feedstock is to be utilized to produce a high quality product that is compatible with the existing distribution system and engine designs.

The fundamental characteristics of biomass (as compared with coal) are given in Table 1. As indicated, biomass contains a higher hydrogen/carbon and oxygen/carbon ratio but lower sulfur and ash content. The heating value for biomass is lower (due to the oxygen content) but the volatile matter content is higher. Thus, except for the oxygen content, biomass exhibits more attractive characteristics than coal for producing a liquid hydrocarbon fuel (less hydrogen source addition, less sulfur and ash removal, milder operating conditions). To address the oxygen problem, an indirect liquefaction approach was chosen for study at ASU. The basic steps are: (1) gasification of the biomass in a circulating solid fluidized bed system to a synthesis gas containing primarily hydrogen, carbon monoxide, ethylene, methane and carbon dioxide, and (2) conversion of the synthesis gas to a liquid hydrocarbon fuel in a catalytic reactor. The oxygen in the biomass is thus converted to carbon monoxide, carbon dioxide and some water in the gasification step. In the liquefaction step, the carbon monoxide is converted to paraffinic hydrocarbons, water and normal propanol via the following possible reactions:

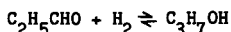
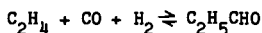
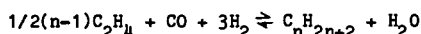
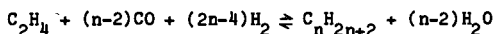


Table 1. COAL AND BIOMASS COMPOSITION (WEIGHT %)

	<u>Coal</u>	<u>Biomass</u>
C	70-80	35-55
H	4-6	4-6
O	5-20	25-50
N	0.5-2	<0.5
S	1-5	<0.5
ash	5-30	0-10
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Heating values (Btu/lb) (dry basis)	9500-15000	6500-9500
Volatile matter, wt. %	30-50	60-90

With proper manipulation of the above reactions, the oxygen in the biomass will end up in water, carbon dioxide and normal propanol. Carbon dioxide and water will be vented from the gasification system regenerator and an immiscible alcohol-water phase will be separated from an oxygen free paraffinic hydrocarbon phase. Past and present efforts on the project have been aimed at optimizing the implementation of this scheme via feedstock assessment, factor studies and operational reliability/control improvements. The individual steps have been studied as well as the integrated system. This paper will address recent studies on the liquefaction system. A range of synthesis gas composition produced in the laboratory in the gasification step (for approximately 100 different feedstocks and a range of operating conditions) is as follows (mole%):

hydrogen	10-45
carbon monoxide	15-60
ethylene	5-40
methane	10-45
ethane	1-5
carbon dioxide	0-15

To a certain extent, the synthesis gas composition is feedstock dependent. However control is possible with operating condition manipulation in the gasification step with the major factors being temperature, steam/biomass ratio and choice of solid in the fluidized bed system. Details on the gasification step can be found elsewhere (1,2).

#### LIQUEFACTION SYSTEM

The catalyst candidates chosen for study fall into two categories: (1) iron, and (2) cobalt. Iron is the traditional active ingredient when performing conversion studies with a synthesis gas dominated by carbon monoxide and hydrogen (3). However biomass offers the opportunity to produce a significant amount of unsaturated gases (primarily ethylene). For this case, cobalt based catalysts are attractive candidates due to the relatively high activity for olefin conversion (as opposed to the relatively inert behavior of iron). Initial liquefaction studies at ASU were performed in a fluidized bed mode. However, primarily motivated by the control complexity of operating fluidized beds in series, a slurry phase system was selected for study as an alternative. In addition to residence time (velocity control) flexibility, the slurry reactor offered the following potential advantages:

- superior temperature control
- longer catalyst life
- catalyst configuration flexibility
- superior gas distribution

The potential disadvantages were increased process complexity (slurry liquid storage and distribution) and possible slurry liquid composition stability problems.

The catalyst and liquid candidates selected for study are listed in Tables 2 and 3. Selection was based on literature guidance, physical and chemical property considerations and system compatibility. All work was performed in a bubble column reactor configuration. Reaction system details and operating procedures are described elsewhere (4,5). The experimental strategy is depicted in Figure 1.

#### RESULTS

Base operating condition screening runs resulted in the selection of following catalyst/slurry liquid combinations for additional study: (1) 25 Co/175 Al<sub>2</sub>O<sub>3</sub> in Fisher paraffin oil, and (2) 48 Fe/4.8 Cu/47.2 kieselguhr in Chevron Refined Wax 143.

Results of fractional factorial experiments to study the effect of reactor operating conditions on product yields for the cobalt study are given in Table 4. Iron catalyst factorial experiment results are shown in Table 5. Note that the feed composition did not include ethylene for the iron study since olefins are essentially inert in the presence of iron. Factor choice and levels were guided by the literature and ASU laboratory experience. Example product compositions for the two studies are shown in Figures 2 & 3. Data was obtained over a sufficient period of time (>8hrs) to insure steady state operation. Base point replication indicated an experimental error<sup>1</sup> of 2% for the cobalt study and 5% for the iron study. Mass balance closures (mass out/mass in x 100) were in the 95-105% range for the two studies.

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Table 2  
Catalyst Candidates

Cobalt/Alumina  
Cobalt Oxide Powder  
Cobalt Oxide Precipitate  
Cobalt-Potassium/Alumina  
Iron-Copper-Potassium Precipitate  
Girdler C-73-1 (Iron Based Ammonia Synthesis Catalyst)  
Iron-Copper/Kieselguhr  
Iron-Copper/Alumina  
Iron-Copper-Potassium/Alumina  
Iron-Copper Precipitate

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Table 3  
Slurry Liquid Candidates

Product Liquid  
Commercial No. 2 Diesel  
Mineral Oil/Paraffin Oil  
Chevron 143 Refined Wax  
Synthetic Motor Oil (Mobil One)  
Tetralin  
Tetraethylene Glycol  
Dimethyl Naphthalene  
Hexadecane  
Triethylene Glycol  
1-Octadecene  
Diethyl Phthalate  
Dow 210H  
Dow Syltherm 800  
Alpha Eicosane  
Revco Mineral Motor Oil

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Mathematical models were fitted to the experimental data for each study, optimized and experimentally verified. Verification of predicted optimums were mixed, dependent on the particular problem posed. Thus close agreement was achieved in some cases while other problems resulted in deviations in both high and low directions. Additional product analyses were performed (eg, heating value, cetane index, API gravity, average molecular weight, most abundant carbon number, grouped composition, Shulz-Flory analysis). Also equilibrium calculations were performed. Composition analysis on the slurry liquids did not indicate any appreciable degradation in the presence of the catalysts although total operating time length was not extensive. Catalyst activity was also stable for the prescribed run lengths.

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<sup>1</sup> exp. error=  $\frac{\text{base point product yield range}}{\text{factorial product yield range}} \times 100$

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Table 4  
Cobalt Study Results<sup>1</sup>

Factors		Feed Gas Comp(mole%) <sup>2</sup>			Responses			
T, °C	P, psia	H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CO	Gas Conversions		Product Yield	
Factorial Pts:					H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CO (mg/gcat/hr)	
310	95	20	5	20	55.8	87.2	36.1	9.7
210	95	40	5	40	28.6	46.6	7.6	2.9
210	95	20	25	40	22.7	13.6	3.4	3.7
310	95	40	25	20	61.7	89.0	37.6	27.0
210	295	40	25	20	28.2	39.6	12.8	82.0
310	295	20	25	40	75.9	80.6	6.4	166.0
310	295	40	5	40	68.8	87.9	39.3	85.0
210	295	20	5	20	13.0	38.6	5.2	11.0
Base Pt.								
260	195	30	15	30	42.0	62.6	13.7	53.0
260	195	30	15	30	50.1	68.0	15.8	50.0
260	195	30	15	30	51.3	69.5	18.3	53.0

<sup>1</sup> experiment: 2<sup>5-2</sup> (2 level, 5 factor)  
fractional factorial with base point replication.  
Superficial gas velocity = ~ 1.0 cm/sec at T,P

<sup>2</sup> balance of gas = carbon dioxide + methane

Table 5  
Iron Study Results<sup>1</sup>

Factors		H <sub>2</sub> /CO		Catalyst Amount		Responses	
T, °C	P, psia	(molar)	(wt. frac.)			Gas Conversions	
Factorial Pts:						H <sub>2</sub>	CO
220	120	0.5	0.05			5.2	0.10
300	120	0.5	0.05			66.4	44.4
220	200	0.5	0.05			1.1	1.1
300	200	0.5	0.05			71.0	46.9
220	120	2.5	0.05			1.2	3.6
300	120	2.5	0.05			32.2	76.7
220	200	2.5	0.05			1.5	5.1
300	200	2.5	0.05			43.3	88.5
220	120	0.5	0.20			2.4	10.0
300	120	0.5	0.20			68.4	24.2
220	200	0.5	0.20			5.4	1.0
300	200	0.5	0.20			54.1	54.9
220	120	2.5	0.20			11.3	18.7
300	120	2.5	0.20			26.6	50.5
220	200	2.5	0.20			9.0	19.7
300	200	2.5	0.20			45.7	49.8
Base Pts:							
260	160	1.5	0.125			41.0	77.0
260	160	1.5	0.125			56.0	81.0
260	160	1.5	0.125			38.1	87.9

<sup>1</sup> experiment: 2<sup>4</sup> (2 level, 4 factor)  
full factorial with base point replication.  
Superficial gas velocity = ~ 1.0 cm/sec at T,P

<sup>2</sup> balance of gas = CO<sub>2</sub> + methane (H<sub>2</sub> + CO = 50 mole %)

## SUMMARY AND CONCLUSIONS

The following assessment of the results presented in the preceeding section is offered:

- (1) For the cobalt study, the order of importance of the factors studied with regard to effect on product yield is as follows (via analysis of variance): temperature, pressure, ethylene, hydrogen, carbon monoxide. For the iron study, the order of importance of the factors is as follows: temperature,  $H_2/CO$ , catalyst amount, pressure.
- (2) Product compositions and properties are attractive and potentially competitive with commercial fuels such as No. 2 diesel and aviation fuels. Product composition is relatively insensitive to operating condition changes with a fixed catalyst.
- (3) Cobalt based catalysts are preferred if a significant amount of olefins are present in the synthesis gas. Without significant olefins, iron catalysts should be considered.
- (4) Product yield improvement potential is considerable via adjustment of catalyst, slurry liquid and reactor operating variable factors via optimization studies.
- (5) The slurry reactor is an advantageous system with regard to temperature control, residence time flexibility and possibly catalyst life. A major disadvantage is the complexity of an additional ingredient in the system (if the product liquid is not utilized).
- (6) Catalyst and liquid life endurance testing need to be performed on the catalyst/liquid systems reported in this paper.

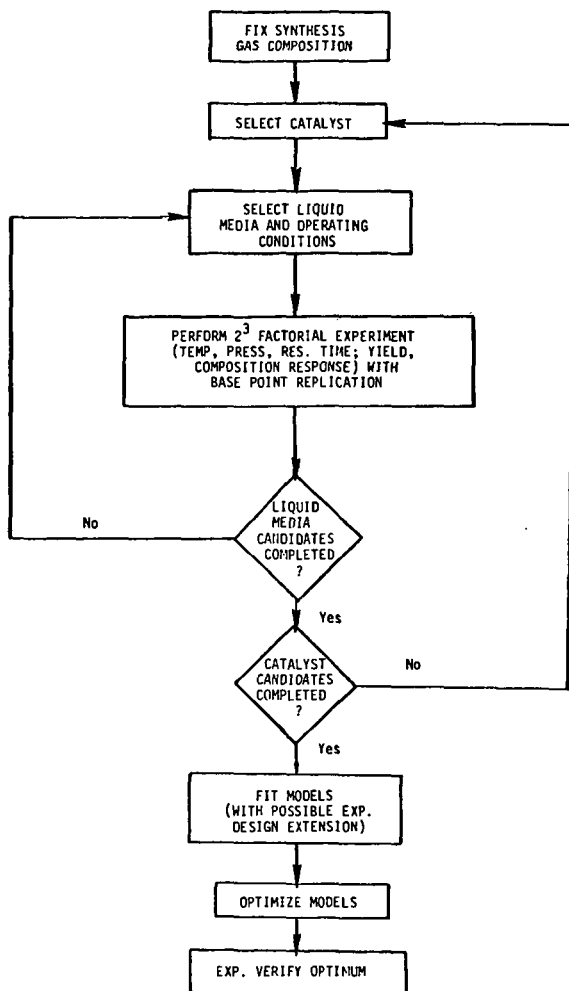
## ACKNOWLEDGEMENTS

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Figure 1  
EXPERIMENTAL PLAN



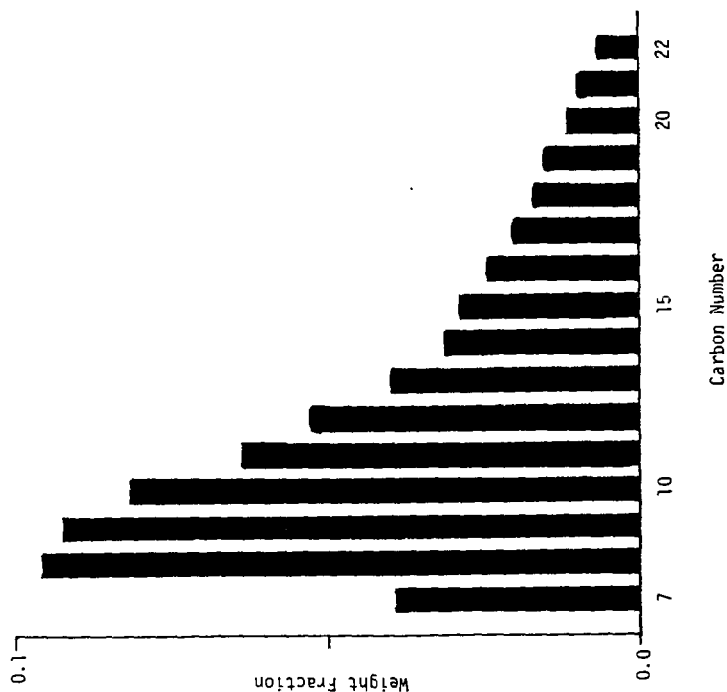


Figure 2  
Organic Product Distribution--Iron Catalyst  
Feed Composition: 26%  $H_2$ , 32%  $CO$ , 16%  $CO_2$ , 13%  $CH_4$ , 13%  $C_2H_4$  (mole %)  
Temperature: 260  $^{\circ}C$   
Pressure: 160 psig  
Superficial velocity: 1 cm/sec at T,P

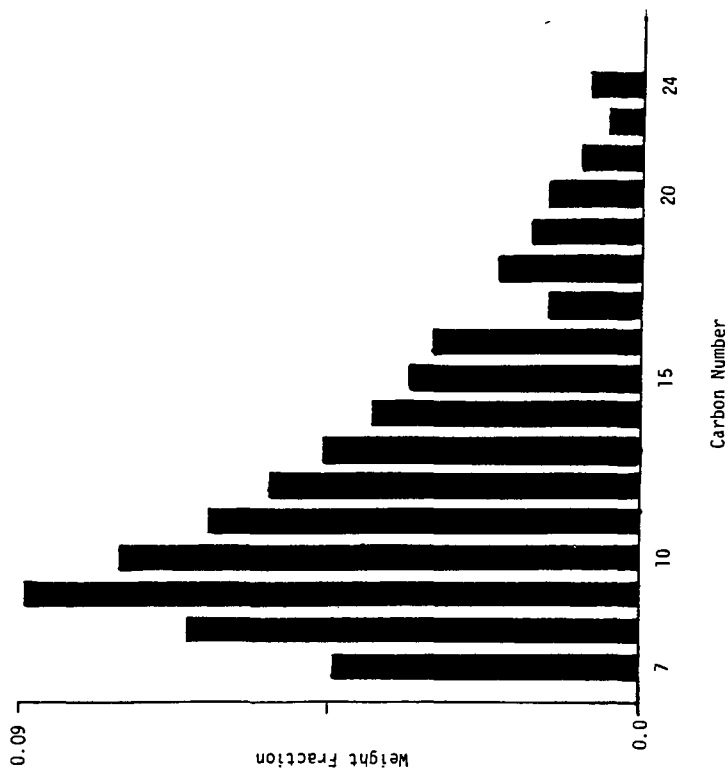


Figure 3  
Organic Product Distribution--Cobalt Catalyst  
Feed Composition: 26% H<sub>2</sub>, 32% CO, 16% CO<sub>2</sub>, 13% CH<sub>4</sub>, 13% C<sub>2</sub>H<sub>4</sub> (mole-%)  
Temperature: 260 °C  
Pressure: 160 psig  
Superficial velocity: 1 cm/sec at T,P